GEORGIA INSTITUTE OF TECHNOLOGY — OFFICE OF CONTRACT ADMINISTRATION

PROJECT ADMINISTRATION DATA SHEET

[X] ORIGINAL [ ] REVISION NO. _____

Project No. G-33-634 (R5947-0A0) GTRC/~~GTX~~ DATE 7 / 31 / 85

Project Director: R. F. Browner School/~~Lab~~ Chem

Sponsor: National Science Foundation

Type Agreement: Grant CHE-8503090

Award Period: From 7/1/85* To 10/31/88** (Performance) 1/31/89 (Reports)

Sponsor Amount:	This Change	Total to Date
Estimated: $		$ 298,600
Funded: $		$ 116,600

Cost Sharing Amount: $ 8,908 Cost Sharing No: G-33-391

Title: Sample Preparation and Introduction for Analytical Atomic Spectroscopy (Chemistry)

ADMINISTRATIVE DATA OCA Contact John Schonk x4820

1) Sponsor Technical Contact:

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Defense Priority Rating: N/A Military Security Classification: N/A

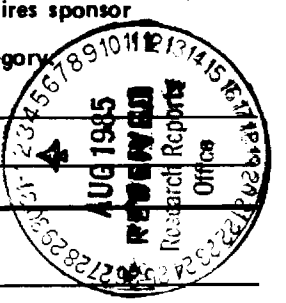
(or) Company/Industrial Proprietary: N/A

RESTRICTIONS

See Attached NSF Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT



COMMENTS:

An advance budget was set up for this project.

*Preaward costs from 5/16/85 have been approved through OPAS.

**Includes 6 month unfunded flexibility period. No funds may be expended after 10/31/86.

COPIES TO: SPONSOR'S I. D. NO. 02.107.000.85.041

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FORM OCA 65:285

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Date 4/13/89

Project No. G-33-634 Center No. R5947-0A0

Project Director R. F. Browner School/Lab Chem.

Sponsor National Science Foundation

Contract/Grant No. CHE-8503090 GTRC XX GIT ____

Prime Contract No. ____

Title Sample Preparation and Introduction for Analytical Atomic Spectroscopy (Chemistry)

Effective Completion Date 10/31/88 (Performance) 1/31/89 (Reports)

Closeout Actions Required:

____ None
____ Final Invoice or Copy of Last Invoice
__X__ Final Report of Inventions and/or Subcontracts - Patent questionnaire sent to P/I
____ Government Property Inventory & Related Certificate
____ Classified Material Certificate
____ Release and Assignment
____ Other ____

Includes Subproject No(s). ____

Subproject Under Main Project No. ____

Continues Project No. ____ Continued by Project No. ____

Distribution:

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G-33-634

Research Proposal Submitted to the National Science Foundation

Technical Report on Grant No. CHE-8503090

SAMPLE PREPARATION AND INTRODUCTION FOR ANALYTICAL ATOMIC SPECTROSCOPY

Principal Investigator: Richard F. Browner

Georgia Institute of Technology

School of Chemistry

Atlanta, GA 30332

SUMMARY OF ACCOMPLISHMENTS UNDER CURRENT GRANT

DURING PERIOD FROM 07.01.85

The primary focus of our current work under the grant is directed towards five major areas in inductively coupled plasma emission spectroscopy: (1) Development and characterization of monodisperse aerosols as sample introduction media for the ICP (2) use of monodisperse and desolvated aerosols for fundamental studies of sample/plasma interaction kinetics (3) development of empirical equation for pneumatic nebulizers as replacement for Nukiyama and Tanasawa equation (5) studies with hydride vapor generation introduction.

This research has resulted to date in four research papers either accepted or submitted for publication, and four conference presentations. These are listed on page 7 of this report

1. Development and Characterization of Monodisperse Aerosols as Sample Introduction Media for the ICP

Liquid sample introduction to plasmas is still predominantly carried out through the use of aerosols, generated with pneumatic nebulizers. The last five years have seen the advent of a number of new designs, all incorporating some degree of novelty, but all providing only marginal improvements in various aspects of the sample introduction process. This lack of progress is a predictable consequence of the application of a purely empirical approach.

In our program, we have developed a unique monodisperse aerosol generator (MAG) which is extremely simple to operate, and allows complete control over the

size of the generated aerosol drops. This device is to be contrasted with the Hieftje isolated droplet generator, which generates much larger drops than our device, and which requires a piezoelectric oscillator to produce the aerosol. The MAG is purely mechanical in operation, relying on natural forces to cause breakup of a high velocity liquid stream. Gas is only introduced to the drop stream to disperse the drops, and prevent agglomeration.

Our present studies with this device have lead to a greatly simplified construction to the generator, which now itself has essentially zero dead volume. This greatly improves cleanout time, and minimizes peak broadening from injected liquid chromatographic and flow injection samples. The device now uses fused silica capillary tube for the nozzle, which improves blockage freedom greatly, and makes the selection of nozzle diameter very simple.

We have recently run preliminary studies with the MAG to determine its analytical utility in ICP emission spectrometry. Initial results were obtained with relatively large drops, in the range 40 - 50 micrometers diameter. There was a substantial improvement of signal and detection limits for the 40 micrometer diameter drops compared with normal pneumatic nebulizer sample introduction. Generally, improvements of one order of magnitude were obtained. With 50 micrometer diameter drops, the detection limits were slightly poorer than with conventional sample introduction.

Our work is currently focusing on the introduction of drops in the range 40 - 10 micrometers in diameter, as part of a systematic search for the optimum drop size for sample introduction for the ICP.

We will shortly take delivery of a Malvern Fraunhofer laser diffraction particle sizing instrument. This will enable us to characterize certain aspects of the MAG

much more readily than we can at present. In particular, it will allow us to optimize the operation of the generator in a far more systematic and rapid manner.

2. Use of Monodisperse and Desolvated Aerosols for Fundamental Studies of Sample/plasma Interaction Kinetics

In order to obtain optimum performance with aerosol introduction to plasmas, it is essential to have detailed knowledge of the solvent and solute vaporization kinetics. This requires the ability to control independently both the solvent loading to the plasma and also the drop size of the aerosol introduced. This latter parameter can now be readily controlled by the use of the MAG. Furthermore, the monodispersity of the aerosol makes calculations of kinetics much easier, in comparison with the difficulties associated with deconvoluting data from a polydispersed aerosol.

The ability to control solvent loading independently of analyte loading is essential to these studies, as the plasma excitation properties change dramatically with even a moderate change in solvent loading. For example, a doubling of solvent loading over conventional introduction can easily cause a signal reduction of two orders of magnitude. For this reason, we have made use of electrothermal vaporization sample introduction to the ICP in some of our studies. By introducing sample to the ICP in the form of both wet and dry aerosol, such that the final desolvated drop size is similar in both instances, it is possible to determine the influence of solvent on plasma properties. Preliminary studies have shown that vaporization kinetics are indeed significantly altered through the presence or absence of solvent in the aerosol drop. Solvent vapor seems to have much less importance on the excitation process. In these studies, the use of high resolution height profiles obtained with a photodiode array have proved invaluable.

3. Development of Empirical Equation for Pneumatic Nebulizers as Replacement for Nukiyama and Tanasawa Equation

In order to put together a useful and complete model for aerosol transport, it is essential to have a reliable model for aerosol generation. Up to this point, all workers have had to rely on the empirical equation developed by Nukiyama and Tanasawa. We have recently made preliminary studies of the primary (i.e. direct from the nebulizer) aerosol produced by a typical pneumatic nebulizer, using borrowed laser scattering equipment. From these early experiments, two very important points become clear: (1) the aerosol drop size distribution is **not** very accurately described by the Nukiyama and Tanasawa equation (2) the aerosol generated by a typical pneumatic nebulizer is very heterogeneous, and so the microscopic rather than just the macroscopic properties must be considered in order to properly describe its behavior.

At present, we are working on the development of curve-fitting routines to allow us to describe the large body of data that we anticipate will be generated shortly after the arrival of the Malvern laser scattering instrument. We have so far determined that a reasonable degree of fit is obtained, again from the preliminary data which may need revision, to a lognormal distribution function. This is not surprising, in view of the ubiquitous use of this function in describing naturally occurring aerosols. However, it does differ from the model proposed by Nukiyama and Tanasawa, who worked with a logarithmic function for primary aerosols.

We anticipate that this work will have fundamental importance in atomic spectrometry. Additionally, its ramifications extend into many more general areas of science. There is presently no model for aerosol generation superior to the Nukiyama and Tanasawa relationship, which we know to be at best only partly correct. A new, and more accurate model is therefore long overdue.

4. Studies with Hydride Generation

There is a significant need in the area of water analysis for rapid, routine determination of As, Sb and Se. Traditionally, this is accomplished with hydride generation on three dedicated atomic absorption instruments. This is a time consuming and expensive process. As a consequence we, in conjunction with the Doraville branch of the USGS, have been making fundamental studies with hydride generation for ICP spectrometry, with a view to developing rapid simultaneous analysis of water samples for the three needed elements. The approach has been to develop an inexpensive three-channel instrument that will work with an inductively coupled plasma source, with flow injection sample introduction.

Preliminary studies have been focused on simplex optimization of the hydride introduction system with the ICP, using conventional optics (Perkin-Elmer 5500 ICP) and continuous sample flow. Our current work has moved to the construction of a dedicated, computer-interfaced three-channel spectrometer system. Tests have demonstrated excellent performance, with detection limits for all elements at about 1 part per billion. This is more than adequate for monitoring water quality. The current experiments involve testing the computer link to the spectrometer, and the introduction of samples by flow injection, which should increase the sample throughput substantially over batch introduction.

RESEARCH PUBLICATIONS DURING CURRENT GRANT PERIOD

1. "System Optimization For The Automatic Simultaneous Determination Of Arsenic, Selenium, And Antimony, Using Hydride Generation Introduction To An Inductively Coupled Plasma," Grace S. Pyen, Stephen E. Long, and Richard F. Browner, Appl. Spectrosc., in press.

2. "Influence Of Water On The Spatial Excitation Behavior Of Selected Elements In The Inductively Coupled Plasma," Stephen E. Long and Richard F. Browner, Spectrochim. Acta B, in press.

3. "Fundamental Sample Introduction Studies Of A Graphite Rod Electrothermal Vaporization Device In Inductively Coupled Plasma Atomic Emission Spectrometry," Susan M. Schmertmann, Stephen E. Long, and Richard F. Browner, J. Analyt. Atom. Spectrosc., submitted.

4. "Influence of Solution Uptake Rate On Signals In Inductively Coupled Plasma Atomic Emission Spectrometry," John Farino, Jonathan Miller, David D. Smith and Richard F. Browner, Appl. Spectrosc., submitted.

5. "Role of Water In The ICP: Part I Fundamental Effects," Stephen E. Long and Richard F. Browner, Spectrochim. Acta B, submitted.

Statement of Funds Estimated to Remain at End of Current Grant Period

It is anticipated that no funds will remain unexpended or uncommitted at the end of the current grant period (April 30, 1986).

CURRENT AND PENDING RESEARCH SUPPORT

	A Source	B Title	C Amount	D Period	E Person Months Acad	E Person Months Summ	F Location
I. Richard F. Browner							
A. Current Support	NSF	1	$116,600	6/01/85-4/30/86	__	1	Ga Tech
	DOE	2	$214,500	9/01/85-8/31/88	—	2	Ga Tech
B. Proposals Pending							
1. This proposal	NSF	1	$91,000	5/01/86-3/31/87	—	1	Ga Tech
2. Other proposals pending	NONE						
3. Proposals to be submitted in the near future	NSF	3	$320,000	9/01/85-8/31/88	—	1	Ga Tech
	Co-Principal Investigator: J. deHaseth, University of Georgia, Dept. of Chemistry						
III. Transfer of Support	NONE						
IV. Other agencies to which this proposal will be submitted	NONE						

Titles of Proposals

1. "Sample Preparation and Introduction for Analytical Atomic Spectroscopy" - This proposal.

2. "Fundamental Studies with a Monodisperse Aerosol-Based Liquid Chromatography/Mass Spectrometry Interface (MAGIC-LC/MS)" - The

direction of this research, involving LC/MS interfacing, is clearly substantially different from the NSF funded work. However, the work with monodisperse aerosols occupies common ground between the this proposal and the work funded by NSF. This extends both to theoretical considerations and to experimental techniques. The net result has been of substantial benefit to both projects.

3. "Monodisperse Generation Interface for Liquid Chromatography / Fourier Transform Infrared Spectrometry (MAGIC-LC/FTIR)" - The studies proposed for FTIR interfacing would bear a similar relationship to the NSF funded work as the LC/MS currently does.

SUMMARY OF ACCOMPLISHMENTS UNDER CURRENT GRANT DURING PERIOD FROM 05.01.86

Work under the grant has been directed towards five major areas of research with the inductively coupled plasma. These are: (1) studies correlating analyte transport properties with analytical signals and interferences (2) use of monodisperse aerosols for fundamental studies of sample/inductively coupled plasma interactions (3) studies with the drop-size characterization of aerosols generated from pneumatic and other nebulizers (4) studies with hydride vapor generation introduction. Additionally, the research has been broadened to encompass a new research area (5) the study of sample introduction processes in inductively coupled plasma mass spectrometry.

The program in the current year has resulted in a total of five publications, including two in press, and seven conference presentations, including a Plenary lecture at the 1987 Winter Conference on Plasma and Laser Spectrochemistry, Lyon, France. Details of publications are given on page 5 of this report.

1. Analyte Transport Properties, Signals and Interferences

A key component in our research has been the continuing attempt to correlate the magnitudes of analytical signals and interferences with various aspects of aerosol transport properties. Important properties include mass transport rate, drop size distribution and solvent mass transport. Even such apparently simple phenomena as the influence of solution uptake rates on signals and interferences in ICP optical emission spectrometry (ICPOES) turn out to be quite complex. Consequently, our studies have been directed towards unraveling the underlying phenomena that relate sample introduction processes with signals and interferences.

We have carried out an extensive study of the influence of solution uptake rate on analytical ICP signals for a selected range of elements (Na, Cu, Mg and Mn) at both atom and ion lines (where appropriate) in order to correlate mass transport trends with the magnitudes of both signals and plasma background. A number of different ICP nebulizers, of both concentric and crossflow design have been examined.

This work assumes considerable practical importance because of the unknown significance of solution pumping in ICP spectrometry. Our work has shown that on the one hand when emission signal alone is considered, very contradictory trends are observed. On the other hand, when signal-to-background ratios are considered the trends generally become predictable, both between elements and between nebulizers. The postulated reason for this difference between signal *vs.* uptake rate and signal-to-background *vs.* uptake rate is related to the influence of solvent loading on the plasma temperature, and hence on its excitation properties. By considering signal-to-background *vs.* signal, the influence of the variation in solvent mass loading on the plasma is largely compensated for.

An additional part of this research has involved a study of interference effects resulting from the presence of high concentrations of common acids, such as nitric, sulfuric and phosphoric acids. The presence of these acids often causes significant interferences in ICPOES, and is not always readily compensated for by the use of internal standards. Our studies, which involved careful mass transport measurements, showed conclusively that previous explanations of the basic mechanisms of acid interference were incorrect. The variation of uptake rate with increasing solution viscosity was shown *not* to be the primary cause of the interferences. In fact, when the uptake rate was controlled with peristaltic pumping, significant interference effects were still present.

By studying aerosol properties, it was shown that the main effect of high acid concentrations was to change the *aerosol drop size distribution*, irrespective of uptake rate, and this drop size change was the primary cause of the observed interferences. In other words, the use of solution pumping was inherently incapable of removing the interference effect.

2. Fundamental Studies With Monodisperse Aerosols

We have carried out extensive studies with the monodisperse aerosol generation (MAG) device. This aerosol generator has the unique property of allowing the generation of dense aerosols with narrow, selectable drop sizes. This is in sharp contrast to the aerosols generated by typical pneumatic nebulizers, which have a broad drop size distribution which extends from submicron diameters to in excess of 100 μm diameter. These studies have been part of an attempt to determine the role of drop size on the vaporization and excitation processes in ICP optical emission spectrometry.

The first part of these studies have involved the detailed characterization of the operation of the MAG as an aerosol generation device, using our Malvern laser Fraunhofer aerosol sizing equipment. This instrument has provided us with a powerful tool for the rapid sizing of *primary* aerosols (*e.g.* the aerosols at the moment of generation, before modifying processes become active). In these studies, we have used a number of primary orifice diameters, solvent types, and gas and liquid flows. From this, we have been able to corroborate our earlier, and more limited studies, which indicated that the primary aerosol produced by the MAG was approximately 2x the orifice diameter for aqueous solvents. We have also shown that it is possible to cause a *secondary* fragmentation process through the use of a high velocity gas stream perpendicular to the liquid flow, which reduces the mean drop size substantially, but also broadens the drop size distribution substantially.

The use of the MAG as a sample introduction device for ICP spectrometry has been studied, and it has shown considerable promise for direct LC/ICP coupling. The benefits include minimal dead volume, and hence very little chromatographic peak broadening, and generally improved detection limits for many elements. The improvement is typically a factor of two.

The use of the MAG for studying the influence of drop size on ICP signals has not initially provided any clear-cut data. This is as a consequence of the aerosol modifying properties of transfer tubes from the MAG to the ICP torch, which have distorted the drop size distribution reaching the plasma from that originally generated by the MAG. A study of this problem is currently underway, and we hope to correct it shortly.

3. Drop Size Distributions of Aerosols: Fundamental Studies

One of the current limitations in sample introduction studies in analytical atomic spectrometry, is the lack of any reliable predictive models. A key factor here is the need for an accurate equation to describe the primary aerosol generation step. The venerable Nukiyama and Tanasawa equation is still the only predictive model available, in spite of its remoteness from the situation applying atomic spectrometry nebulizers. We have embarked on a preliminary systematic study of aerosol generation with a number of representative nebulizer types, including crossflow and concentric versions. We have also considered the influence of gas and liquid flows, solvent surface tension and viscosity, and the spatial characteristics of the aerosols generated.

A preliminary analysis of the data has shown some extremely interesting trends: (1) It is clear that the *numerical* predictions of the Nukiyama and Tanasawa equation for mean drop size are quite inappropriate for nebulizers in current use in atomic spectrometry. (2) While the predicted influence of gas flow on mean drop size is in the correct direction *(e.g.) higher gas flow gives rise to smaller diameter drops*, the *magnitude* of the

effect is much less than predicted. (3) There appears to be very little influence of liquid flow on drops size distributions.

Further, much more extensive, studies are currently underway in order to develop an empirical aerosol generation equation of general predictive value to atomic spectroscopists.

4. Hydride Generation Studies

There is a strong need, particularly in environmental studies, for an improved general procedure for monitoring trace levels of As, Sb and Se. As part of a collaborative study with the Atlanta branch of the USGS water analysis laboratories, we have developed a novel instrument for the simultaneous determination of the above elements in water samples. The instrument fits on to a conventional ICP source, and provides simultaneous three-channel detection of As, Sb and Se at the ppb level. Detection limits, under simplex optimized conditions, were approximately 1 ppb for all elements. The developed system is a continuation of earlier studies with hydride generation that we have carried out. It also incorporates the ability to use either continuous or flow injection sample introduction. A detailed comparison of these two modes of sample introduction was undertaken as part of the study. An instrument based on the concepts developed is currently in use at the USGS Denver laboratories.

5. ICP/MS Sample Introduction Studies

We have been able to obtain the loan of a PlasmaQuad ICP/MS instrument from VG Isotopes, Ltd. This has allowed us during the last nine months to extend our studies of sample introduction into this new field. We have carried out extensive research into the influence of sample introduction properties on ICP/MS performance, in comparison to the influence on ICPOES performance. The coupling between the sample introduction train and the mass spectrometer quadrupole (*e.g.* aerosol → salt particles → ions → MS interface) has been shown to be closely interactive. This contrasts with the situation in ICPOES, where photons leave the plasma in a manner totally uncoupled to the detection system.

Studies have shown the great importance of nebulizer gas flow on the magnitude of the ion count, and have also shown that there is a close interrelation between gas flow, incident RF power, and ion count. Studies for a range of elements with widely differing masses have shown that it is possible to arrive at one compromise set of conditions of power and gas flow which provides uniformly good response for all elements. This is a vitally important conclusion for the future development of ICP/MS as an anlytical technique, as it makes its widespread use in a true multielement mode operationally feasible.

Other studies of great importance to the sample introduction aspects of ICP/MS are currently underway. The role of both analyte mass loading and solvent mass loading on signals and interferences is currently being studies, and this topic shows great promise as an area where major advances can be made in ICP/MS analysis.

RESEARCH PUBLICATIONS DURING PERIOD 05.01.86 - 04.30.87

1. "System Optimization for the Automatic Simultaneous Determination of Arsenic, Selenium, and Antimony, Using Hydride Generation Introduction to an Inductively Coupled Plasma" Grace S. Pyen, Stephen Long, and Richard F. Browner, Appl. Spectrosc. **40**, 246 (1986).

2. "Influence of Water on the Spatial Excitation Behavior of Selected Elements in the Inductively Coupled Plasma," Stephen E. Long and Richard F. Browner, Spectrochim. Acta **41B**, 639 (1986).

3. "Investigation of Parameters with a Quadrupole ICP/MS", G. Zhu and R. F. Browner, Appl. Spectrosc., Feature article, scheduled March 1987.

4. "Influence of Solution Uptake Rate On Signals In Inductively Coupled Plasma Atomic Emission Spectrometry," John Farino, Jonathan Miller, David D. Smith and Richard F. Browner, Anal. Chem., (1987), in press.

5. "Fundamental Studies of a Graphite Rod Electrothermal Vaporization Device for Inductively Coupled Plasma Atomic Emission Spectrometry", Susan M. Schmertmann, Stephen E. Long and Richard F. Browner, J. Analyt. Atom. Spectrosc., (1987), in press.

CONFERENCE PRESENTATIONS

1. "Studies with Monodisperse Aerosol Introduction in ICP Optical Emission Spectrometry", Arthur J. Faske and Richard F. Browner, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ (1986).

2. "Fundamental Studies of a Graphite Rod Electrothermal Vaporization Device for Sample Introduction in Inductively Coupled Plasma Atomic Emission Spectrometry", Susan M. Schmertmann], Stephen E. Long and Richard F. Browner, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ (1986).

3. "In Search of the Optimum Droplet Size for Inductively Coupled Plasma Emission Spectrometry", Jonathan R. Miller, Stephen E. Long and Richard F. Browner, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ (1986).

4. "Sample Introduction Studies for ICP/MS", 28th Rocky Mountain Conference, Denver, CO (1986), **invited talk.**

5. "Recent Studies with Gas and Aerosol Flows in ICP/MS Spectrometry", Rocky Mountain Mass Spectrometry Users Group, Denver, CO (1986).

6. "Recent Advances in Sample Introduction for ICP Optical Emission Spectrometry", Eastern Analytical Symposium, NY (1986), **invited talk.**

7. "Sample Introduction for ICPOES and ICP/MS", Richard F. Browner, 1987 Winter Conference on Plasma and Laser Spectrochemistry, Lyon, France (1987), **plenary talk.**